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Short-Lived Actinide QA Exercise Results and Summary

(After Action Report)

Exercise: QA-MVSLA-2017-04

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SYNOPSIS

In April 2017 an inter-laboratory exercise entitled *Method Validation for Short-lived Actinide Production and Analysis* (QA-MVSLA-2017-04) was supported by the LANL Radiochemistry and Mass Spectrometry Teams.

Objectives identified for the exercise included:

1) Characterize inter-laboratory data consistency for ^{237}U and ^{239}Np determination via radiometric methods.
2) Characterize intra-laboratory data consistency between radiometric methods and mass spectrometry techniques for $^{237}U/^{237}Np$ and $^{239}Np/^{239}Pu$ parent/daughter radionuclide pairs.
3) Evaluate the acceptability of the $^{10}B_4C$ shielded DU fission spectrum at the Washington State University (WSU) research reactor as a production method for ^{237}U and ^{239}Np.

This after action report (AAR) summarizes all phases of the exercise, which involved radiometric determination of ^{99}Mo, ^{237}U, and ^{239}Np in an irradiated DU foil, radiometric determination of ^{99}Mo and ^{111}Ag in a co-located HEU foil, mass spectrometric determination of ^{237}Np and ^{239}Pu in the same irradiated DU foil after 10 half-lives of parent decay, and mass spectrometric determination of ^{237}Np and ^{239}Pu in an unirradiated DU foil of the same source material.

The DU and HEU foils were dissolved by PNNL and "A" solutions of each were received by LANL on April 13, 2017. The DU foil solutions were assigned a LANL internal exercise ID of 4251, which includes the sample IDs indicated in Table 1 below. The HEU foil solution was assigned an exercise ID of 4252.

Table 1: Samples Included in Exercise 4251

Collection ID	Description
SLA-2017-04-02-DU	Irradiated DU foil solution
SLA-2017-04-02-DU-BLANK	Unirradiated DU foil solution
SLA-2017-04-02-HEU	Irradiated HEU foil solution
LANL2-SLA17-PRS-BLANK	Process blank solution for irradiated DU foil dissolution process at PNNL
LANL2-SLA17MB-PRS-BLANK	Process blank solution for unirradiated DU foil dissolution process at PNNL

STANDARD OPERATING PROCEDURES (WORK INSTRUCTIONS)

The following procedures were followed to complete analysis of the samples in this QA exercise.

Note: Deviations from the procedure are given in the document text. If there are no notes below, the procedure was followed without deviations.

- WI-RC1-307-0004, Molybdenum
- WI-RC1-307-0009, Silver/Cadmium
- WI-RC1-307-0011, Uranium Purification and Electroplating – Deviations described in the text
- WI-RC1-307-0012, Neptunium Purification and Electroplating
- WI-RC45-0005, Cleaning Labware
- WI-RC45-0022, Cleaning Mass Spectrometry Equipment and Supplies
- WI-RC45-0008-1, Pu, Np, Am and Cm Chemistry – Deviations described in the text
- WI-RC45-0023, TIMS Filament Preparation and Loading
- WI-RC45-0025, Routine Operation of TIMS

SAMPLE PROCESS FLOW

RADIOMETRIC SAMPLE PROCESSING

The key radiochemistry measurements for this exercise are focused on determination of ^{237}U and ^{239}Np. For this purpose separate aliquots optimized for sample activity were processed. In the case of ^{237}U, 4 x 1mL aliquots of the "A" solution were purified using the UTEVA extraction chromatography method and assayed as 5mL standard solutions using gamma-ray spectroscopy. The chemical yield was determined using isotope dilution inductively-coupled plasma mass spectrometry (ID-ICP-MS) by using the ratio of uranium concentration in the radiochemically purified fraction compared to the uranium concentration in the dissolved target solution. In the case of ^{239}Np a total of six separate aliquots were processed during the exercise. Immediately upon receipt of the sample, 4 x 0.5mL aliquots were purified beginning April 13, 2017. Approximately a week later two additional 4 mL aliquots were purified for ^{239}Np determination. The ^{239}Np aliquots were first traced with ^{237}Np (NIST 4341), purified using liquid/liquid extraction and ion-exchange chromatography, and then electroplated onto a 1-inch stainless steel disk for assay by gamma-ray spectroscopy. The chemical yield was determined by measurement of the recovered ^{237}Np tracer using alpha spectrometry.

The fissions per gram of "A" solution was determined by measuring the beta activity of ^{99}Mo in purified aliquots. A single measurement was completed for each of the DU and HEU samples. The activity of ^{111}Ag produced in the HEU sample was determined via beta-decay counting for a purified aliquot and is reported as an R-value on a $^{235}U_{thermal}$ basis. A detailed description of each of the above processes follows.

Determination of uranium concentration. Absolute uranium concentrations were determined for aliquots received from the two irradiated uranium samples, SLA-2017-04-02-DU and SLA-2017-04-02-HEU. For each solution, careful analytical dilutions were prepared on April 17, 2017. A known mass of the respective dilution was spiked with a standardized ^{233}U solution and then analyzed using a single collector ICP-MS (Thermo X-series II) equipped with an ESI Apex desolvation nebulizer. Instrumental mass bias was determined and the raw data

corrected using measurements of IRMM 74/1. A comparison of the gravimetric and measured (ID-ICP-MS) uranium concentrations is presented in Table 2.

Table 2. Absolute uranium concentrations.

Collection ID	Target mass (mg)	"A" solution mass (g)	[U] gravimetric (mg/g)	[U] ID-ICP-MS (mg/g)	Gravimetric vs. ICPMS (% difference)
SLA-2017-04-02-DU	437.8	131.9831	3.317	3.310(6)	–0.20
SLA-2017-04-02-HEU	44	110.5739	0.3979	0.3989(7)	+0.24

Determination of ^{237}U. Aliquots of the irradiated DU sample were purified using the UTEVA extraction chromatography method to remove interfering fission products and ^{239}Np from the sample. The purified sample, containing a significant mass (~3.3 mg) of DU target material, was transferred to a 20mL scintillation vial in 5mL of 3M HNO_3. The purified sample solutions were each assayed using gamma-ray spectroscopy with detector calibrations for this type of standard sample geometry. Three particular x-ray and gamma-ray lines listed in Table 3 were used to quantify ^{237}U (97, 101, 208 keV). Although included in the Table, the gamma-ray at 59.5 keV was not used in the analysis. Note also that x-rays at 96.242 and 97.069 keV are not resolved in our system (counter 48) and the abundance for the combined peak was used in data analysis. Gamma counting of the purified samples was started on the evening of April 14, 2017.

Table 3. Prominent X-ray and Gamma-ray Lines associated with ^{237}U decay.

Gamma-ray or X-ray Line (keV)	Abundance (%)
59.5412 (gamma)	34.5(8)
96.242 + 97.069 (x-ray)	0.0583(19) + 15.8(4)
101.059 (x-ray)	25.4(6)
208.00 (gamma)	21.2(3)

Each sample was counted successively at least three times. The purified sample activity and standard deviation is based on these assays, decay corrected to EOB. For example in the case of aliquot 4251-01-027 the measured ^{237}U concentration was 5.01×10^9 (± 1.58%) atoms/sample. This raw measurement was then corrected for decay during irradiation, chemical yield, and normalized to aliquot mass of "A" solution (equation 1). The correction for decay of ^{237}U during neutron irradiation is given by equation 2. For this experiment the neutron irradiation length was 8 hours and the correction is near 1.7%.

$$^{237}U(atoms/g) = \frac{^{237}U(atoms/sample) \times correction_{decay\_during\_irradiation}}{aliquot\_mass \times chemical\_yield} \quad (1)$$

Correction due to decay during irradiation: $\frac{t_{irradiation} \times \lambda_{^{237}U}}{1 - e^{\left(-t_{irradiation} \times \lambda_{^{237}U}\right)}} = 1.017212$ (2)

The uncertainty for each individual analysis represents the combined relative standard deviation of the gamma-ray assay (± ~1.6%), the uncertainty in chemical yield (± 0.26%), and the uncertainty in absolute gamma-ray efficiency calibration (± 2.2%). The chemical yield was determined using ID-ICP-MS by comparing the concentration of uranium in the "A" solution to the concentration of uranium in the purified ^{237}U sample.

The final reported value is the average of the four determinations (Table 4). The uncertainty in this result represents the combined relative standard deviation of the four measurements (± 0.63%), the average relative uncertainty in chemical yield (± 0.26%) and the uncertainty in absolute gamma-ray efficiency calibration (± 2.2%). For this analysis the dominant source of uncertainty is the gamma detector efficiency calibration.

Table 4. ^{237}U Replicate Results.

Sample ID	Aliquot mass (g)	Chemical Yield (%)	^{237}U (atoms/g A)
4251-01-027	1.0884	95.07 (± 0.26%)	4.923 x 10^9 (± 2.7%)
4251-02-027	1.0916	99.46 (± 0.26%)	4.901 x 10^9 (± 2.8%)
4251-03-027	1.0909	99.47 (± 0.27%)	4.903 x 10^9 (± 2.7%)
4251-04-027	1.0882	99.49 (± 0.26%)	4.850 x 10^9 (± 2.8%)
Final average			4.894 x 10^9 (± 2.3%)

Determination of ^{239}Np. Aliquots were processed for ^{239}Np determination in two batches. The first batch was comprised of 4 x 0.5 mL aliquots, and then repeated about a week later (~3 additional half-lives) for 2 x 4mL aliquots. The analytical methods were the same for both batches. Key steps in the purification protocol include first addition of ^{237}Np tracer and equilibration, pre-concentration using LaF_3 precipitation, then selective liquid/liquid extraction of Np(IV). The extraction uses 2-thenoyltrifluoroacetone in *o*-xylene in contact with 1M HCl containing reducing agents NH_2OH•HCl/$FeCl_2$. A final purification employs AG MP-1 (50-100 mesh) anion-exchange resin using the hydrochloric acid system to separate Np from any trace uranium or plutonium that may remain in the sample. Each Np sample was then prepared as a pure electrodeposit onto 1-inch stainless steel planchettes. The samples were assayed using gamma-ray spectroscopy and then the yield determined by alpha counting to quantify ^{237}Np recovery. A number of prominent x-ray and gamma-ray lines are associated with ^{239}Np decay (Table 5). The particular lines and their abundances used in quantifying the concentration of ^{239}Np are 106, 228, and 277.6 keV.

Table 5. Prominent X-ray and Gamma-ray Lines associated with ^{239}Np decay.

Gamma-ray or X-ray Line (keV)	Abundance (%)
99.525 (x-ray)	15.1(3)
103.734 (x-ray)	24.2(5)
106.125 + 106.48 (gamma)	27.2(4) + 0.049(8)
209.753 (gamma)	3.42(5)
226.378 + 227.83 + 228.183 (gamma)	0.28(2) + 0.51(calc) + 10.76(18)
277.599 (gamma)	14.38(21)
315.879 (gamma)	1.60(3)
334.309 (gamma)	2.07(3)

Each sample was counted successively at least three times. The purified sample activity and standard deviation is based on these assays, decay corrected to EOB. For example in the case of aliquot 4251-01-039 the measured ^{239}Np concentration was 2.51 x 10^9 (± 1.78%) atoms/sample. This raw measurement was then corrected for decay during irradiation, chemical yield, and normalized to aliquot mass of "A" solution (equation 3). The correction for decay of ^{239}Np during neutron irradiation is given by equation 4. For this experiment the neutron irradiation length was 8 hours and the correction is almost 5%.

$$^{239}Np(atoms/g) = \frac{^{239}Np(atoms/sample) \times correction_{decay\_during\_irradiation}}{aliquot\_mass \times chemical\_yield} \quad (3)$$

Correction due to decay during irradiation: $$\frac{t_{irradiation} \times \lambda_{^{239}Np}}{1 - e^{\left(-t_{irradiation} \times \lambda_{^{239}Np}\right)}} = 1.049824 \quad (4)$$

The uncertainty for each individual analysis represents the combined relative standard deviation of the gamma-ray assay (range from ± 0.34 to 1.8%), the uncertainty in chemical yield (± 1.0%), and the uncertainty in absolute gamma-ray efficiency calibration (± 2.2%). The chemical yield was determined using alpha spectrometry (ORTEC Ensemble) to measure the activity of ^{237}Np tracer using an absolute detector efficiency calibration tied to an historic LANL gas proportional alpha detection system.

Table 6. ^{239}Np Replicate Results.

Sample ID	Aliquot mass (g)	Chemical Yield (%)	^{239}Np (atoms/g A)
4251-01-039	0.5438	10.34 (± 1.0%)	4.695 x 10^{10} (± 3.0%)
4251-02-039	0.5439	10.53 (± 1.0%)	4.946 x 10^{10} (± 2.8%)
4251-03-039	0.5433	12.81 (± 1.0%)	4.977 x 10^{10} (± 2.8%)
4251-04-039	0.5438	14.59 (± 0.93%)	4.839 x 10^{10} (± 2.4%)
4251-05-039	4.3771	37.84 (± 1.0%)	4.627 x 10^{10} (± 2.4%)
4251-06-039	4.3991	36.02 (±1.0%)	4.665 x 10^{10} (± 2.3%)
Final weighted average			4.734 x 10^{10} (± 3.8%)

The final reported value is the weighted average of the six determinations, in which weighting was based on chemical yield (Table 6). The uncertainty in this result represents the combined relative weighted standard deviation of the six measurements (± 3.0%), the average relative uncertainty in chemical yield (± 1.0%) and the uncertainty in absolute gamma-ray efficiency calibration (± 2.2%). For this analysis the dominant source of uncertainty is the variation in measurement results between the six aliquots.

Weighted standard deviation is somewhat unusual and the formula for this statistic is given by equation 5, taken from a NIST publication,[1] where w_i is the weight for the ith observation, N' is the number of non-zero weights, and $\bar{x}_w$ is the weighted mean of the observations.

$$\text{weighted standard deviation} = \sqrt{\frac{\sum_{i=1}^{N} w_i (x_i - \bar{x}_w)^2}{\frac{(N'-1)\sum_{i=1}^{N} w_i}{N'}}} \qquad (5)$$

MASS SPECTROMETRY SAMPLE PROCESSING

The ^{239}Pu and ^{237}Np progeny of ^{239}U (measured radiometrically as ^{239}Np) and ^{237}U were determined using mass spectrometry from the same sample aliquot. The following description applies to samples SLA-2017-04-02-DU and SLA-2017-04-02-DU-BLANK. The 2 process blanks from sample dissolution provided by PNNL were taken directly to RC-45 and were processed using the normal Pu-Np procedure without deviation.

- [1] Heckert, N. A. and Filliben, James J. (2003). NIST Handbook 148: Dataplot Reference Manual, Volume 2: Let Subcommands and Library Functions", National Institute of Standards and Technology Handbook Series, June 2003.

Sample processing began on June 7, 2017 which was 63 days (~9.3 ^{237}U half-lives) after irradiation to allow for ingrowth of the daughter analytes. Due to the high concentration of both analytes in the irradiated DU sample, a 100x dilution of the A solution was first made. From the diluted solution, 3 x 2g replicates were aliquotted (sample #6-9 through 6-11). The unirradiated DU sample was split into 2 replicates of 13.5 g (sample #6-12) and 21.3 g (sample #6-13).

Because of the high U content in these samples, they could not be immediately taken to the RC-45 clean laboratory at LANL. An initial separation of the Pu and Np to remove as much U as possible was performed in the RC-1 radiochemistry space. This separation was a deviation from the normal mass spectrometry Pu-Np procedure. Spike aliquots of ^{244}Pu and ^{236}Np were taken in the clean lab per the normal operating procedure and were then brought to RC-1 to combine with the sample aliquots and a drop of perchloric acid. The samples were dried overnight. The usual spike equilibration step of fuming the samples + spikes to dryness with 2 ml of perchloric acid was not performed due to lack of a perchloric hood in the RC-1 lab available for this work.

A neodymium fluoride precipitation was then performed to remove uranium using neodymium solution that was previously column purified in the clean laboratory. The spiked samples were combined with 5 mg Nd, 1 ml of saturated hydroxylamine hydrochloride reducing reagent and 6 ml 2M hydrochloric acid. After an hour equilibration, 0.75 ml hydrofluoric acid was added and the precipitate was centrifuged and decanted. The pellet was dissolved in 1 ml saturated boric acid and 1 ml concentrated nitric acid. A quick hand monitor check of the solutions revealed residual radioactivity in the unirradiated DU samples, but none in the irradiated samples. Due to anticipated sample activity, a radiological control area had been set up in the "outside" lab (W108) of the RC-45 clean laboratory. The dissolved solutions were taken to this lab for the remainder of the sample processing which followed the normal mass spectrometry procedure.

The precipitated samples were batched together with the PNNL dissolution blanks once in the RC-45 W108 lab for the regular Pu-Np chemistry. Samples were received in RC-45 on June 12, 2017. They were fumed with 2 ml perchloric acid. A neodymium oxalate precipitation was performed followed by an iron hydroxide precipitation, a 2 ml anion column, and a 200 ul anion column. The final solutions were brought inside the clean labs for normal bead chemistry steps and TIMS filament loading. Samples were measured by TIMS from June 27-29, 2017.

The reported result for the irradiated foil, SLA-17-04-02-DU was the average of the 3 replicates plus/minus 1 sigma standard error of the mean of the replicate measurements. The results of each replicate are shown below.

Table 7. ^{239}Pu-^{237}Np Replicate Results for Irradiated DU

Sample ID	Aliquot mass (g)	^{239}Pu (atoms/g A)	^{237}Np (atoms/g A)	^{237}Np/^{239}Pu
4251-6-9	0.01821	4.95 x 10^{10} (± 0.6%)	5.13 x 10^{9} (±0.9%)	0.104 (±1.1%)
4251-6-10	0.02218	4.90 x 10^{10} (± 0.6%)	4.63 x 10^{9} (±1.0%)	0.094 (±1.2%)
4251-6-11	0.02098	4.96 x 10^{10} (± 0.6%)	4.85 x 10^{9} (±1.0%)	0.098 (±1.1%)
Reported Average (± 1σ SE)		4.94 x 10^{10} (±0.6%)	4.87 x 10^{9} (±3.0%)	0.099 (±2.7%)

The unirradiated foil results were reported differently—from a single measurement value each. At some point during carburization of the beads inside the ARBOS, one of the 2 unirradiated foil beads (sample 6-13) dislodged from the filament and was lost. The filament was measured despite this loss and yielded about 1/3 of the Np-236 spike counts that a "good" sample would yield. The Pu yield was too low to consider usable. Therefore, results for Pu for the unirradiated foil were reported from the remaining bead (sample 6-12) only. Results for Np for the unirradiated foil were reported from sample 6-13 only, due to the smaller size of the 6-12 aliquot, which was at our detection limits and had very high uncertainty. However, the uncertainty for Np on sample 6-13 may be underestimated. It is not typical for beads to be lost, and we do not usually take a measurement on a filament without a bead. Therefore there is no data to characterize the physics of this phenomenon. For example, analyte that diffuses into the rhenium filament from the bead could have a different fractionation during ionization than analyte that is still adsorbed to the remainder of the bead. The discovery that measurable Np remains in the filament after bead loss (but Pu did not in this case) is certainly worthy of more exploration to quantify the accuracy of the data. This finding could be beneficial if it is still possible to glean some sample data from situations where it was thought none remained. The results obtained for the unirradiated foil are shown in the table below:

Table 8. ^{239}Pu-^{237}Np Replicate Results for Unirradiated DU (Matrix Blank)

Sample ID	Aliquot mass (g)	^{239}Pu (atoms/g A)	^{237}Np (atoms/g A)
4251-6-12	13.56	1.21 x 10^{6} (± 0.7%)	<1.4 x 10^{4} *
4251-6-13	21.31	Bead lost, no data	3.0 x 10^{4} (±7%)

*At/below detection limits. Detection limits are 3 standard errors of the mean of the process blank population, scaled to the fraction of sample analyzed.

The mass spectrometry team also measured ^{239}Pu and ^{237}Np in the dissolution blanks provided by PNNL and in a process blank that accompanied the samples in our higher level radiochemistry space (RC-1) used for the neodymium fluoride precipitation. Of the two

dissolution blanks received by LANL from the other lab, the solution LANL2-SLA17MB-PRS-BLANK (the blank accompanying dissolution of the unirradiated foil) was far lower for both analytes. In fact, it was only about twice our typical process blank and was at the upper end of the normal variation for our blank population range. The other dissolution blank, LANL2-SLA17-PRS-BLANK 9which accompanied the dissolution of the irradiated foil) had much higher levels of both analytes and was above our typical process blank range. Similarly, the blank that accompanied samples through the RC-1 radiochemistry space was also above the normal process blank range for the clean labs. However, for this exercise, the process blank that accompanied these samples through only the RC-45 clean labs was also higher than our normal range, especially for Pu. So it is difficult to say for sure whether the elevated values in the blanks arose during dissolution, or during subsequent chemical processing. The levels arise from sample cross-talk with the much higher level samples they accompany, not from dirty lab spaces. We have seen this same cross-talk in every other high level QA exercise we have done to date, because we are measuring multiple orders of magnitude difference between samples and blanks. The elevated blanks are insignificant compared to the irradiated foil results. However, for the unirradiated foil, especially for the very trace Np, some of these blank values are in the same range as the sample value.

Table 9. Mass Spectrometry Blank Results

Sample ID	Aliquot mass (g)	As measured ^{239}Pu (atoms/aliquot)	Normalized ^{239}Pu (atoms/g "A")	As measured ^{237}Np (atoms/aliquot)	Normalized ^{237}Np (atoms/g "A")
PNNL-SLA17-PRS-BLANK	34.17	3.06×10^5 (± 2.4%)	8.13×10^3 * (± 3.0%)	1.76×10^6 (±2.3%)	4.94×10^4 * (±3.7%)
PNNL-SLA17MB-PRS-BLANK	34.44	5.03×10^4 (± 3.5%)	6.4×10^2 * (± 23%)	1.49×10^5 (± 3.6%)	2.1×10^3 * (± 39%)
4251-6-16 RC1-BLANK	1 aliquot	1.08×10^5 (± 2.8%)	N/A	4.78×10^5 (± 2.3%)	N/A
4251-6-17-RC45-BLANK	1 aliquot	9.84×10^5 (± 1.1%)	N/A	1.42×10^5 (± 4.1%)	N/A
RC-45 process blank average	1 aliquot	2.83×10^4 (± 18%)	N/A	7.57×10^4 (± 37%)	N/A

*Value was corrected for the process blank running average value prior to normalization

FINAL REPORTED MEASUREMENT RESULTS

A summary of all LANL results as reported are shown in Table 10

Table 10. As Reported LANL Measurement Results†

Sample ID	[U] (mg/g) via IDICPMS	Fissions/g via $^{99}Mo_{beta}$	^{237}U or ^{237}Np (atoms/g)	^{239}Np or ^{239}Pu (atoms/g)	^{111}Ag R-value
4251-DU (radiometric)	3.310 (± 0.19%)	9.020×10^{10} (± 1.5%)	4.894×10^{9} (± 2.3%)	4.734×10^{10} (± 3.8%)	—
4251-DU (mass spec.)			4.87×10^{9} (± 3.0%)	4.94×10^{10} (± 0.6%)	
4251-DU-BLANK			3.0×10^{4} (±7%)	1.21×10^{6} (± 0.7%)	
4252-HEU	0.3989 (± 0.17%)	6.521×10^{10} (± 1.4%)	—	—	2.80 (± 0.8%)

†Analytical results are reported per gram of "A" solution and are decay corrected to EOB 97.9979 (2017). Half-lives are 6.75 days for ^{237}U and 2.3565 days for ^{239}Np. Uncertainties are 1 sigma.

The reported value for radiometric ^{237}U match within errors the mass spectrometric ^{237}Np, and similarly the radiometric ^{239}Np value matches the mass spectrometric ^{239}Pu value with errors.

DISCUSSION OF PRODUCTION METHOD

The $^{10}B_4C$/WSU research reactor production method can be profitably compared to related critical assembly experiments that have been recently completed at the NCERC test facility in Nevada. Table 11 summarizes key metrics for the two production methods that are relevant to this exercise. In absolute terms the PNNL lead B_4C/WSU reactor production method provided more than an order of magnitude more activity for short-lived radionuclides than were required for this inter-laboratory comparison test. The B_4C/WSU production method appears to be scalable to relatively long irradiation times. In this case the B_4C/WSU irradiation was conducted over 8 hrs compared to 1hr for the FLATTOP critical assembly experiment. If the data is normalized to irradiation time, the new B_4C/WSU reactor method provided approximately a two-fold increase in short-lived radionuclides per hour of irradiation.

Table 11. Production of short-lived actinides and fissions.

Experiment	Irradiation length (hr)	Fissions/mg DU	^{237}U (atoms/mg DU)	^{239}Np (atoms/mg DU)
FLATTOP critical assembly (HEU core)[1]	1	1.90×10^{9}	8.25×10^{7}	1.02×10^{9}
B_4C/WSU	8	2.73×10^{10}	1.48×10^{9}	1.43×10^{10}

[1] *NA-22 funded experiment conducted on April 26, 2017.*

The average neutron spectrum provided by the B_4C/WSU production method can be qualitatively compared to a series of LANL critical assembly irradiations. For this comparison a spectral index can be defined by the ratio of fissions in DU versus fissions in HEU (normalized to mass of target). The spectral index results from the relative change in fission cross-sections for the two materials as a function of neutron energy (Figure 1).

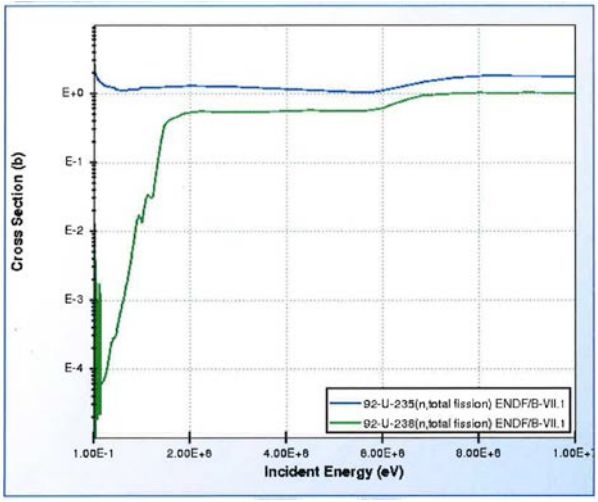

Figure 1. Cross sections for (n, total fission) for U-235 (blue) and U-238 (green).

Similarly the cross-sections for key nuclear reactions in ^{238}U are strongly dependent on average neutron spectrum (Figure 2).

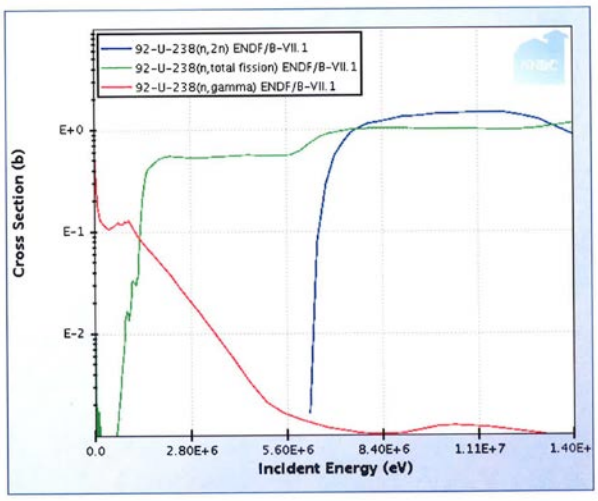

Figure 2. Cross sections for (n, 2n) (blue); (n, total fission) (green); and (n, gamma) (red) for U-238

For each experiment, fissions in DU and in HEU target materials were measured to provide a qualitative spectral index. For the DU target, ^{237}U and ^{239}Np were also measured. A plot of these data compared to the QA-MVSLA-2017-04 data is shown in Figure 3. The comparison indicates that the B_4C/WSU irradiation method provides a relatively high-energy fission spectrum that favors ^{237}U production. For this series of experiments the $^{237}U/^{239}Np$ atom ratio

varies by over a factor of 5 within a range of spectral indices that are all considered "fission spectrum". These modest differences in so-called fission spectrum are readily detected in the $^{237}U/^{239}Np$ ratio. The average measurement uncertainty in the $^{237}U/^{239}Np$ ratio is ~4%, but is trivial compared to the large variation in absolute $^{237}U/^{239}Np$ ratio due to the critical assembly configuration and resulting neutron spectrum.

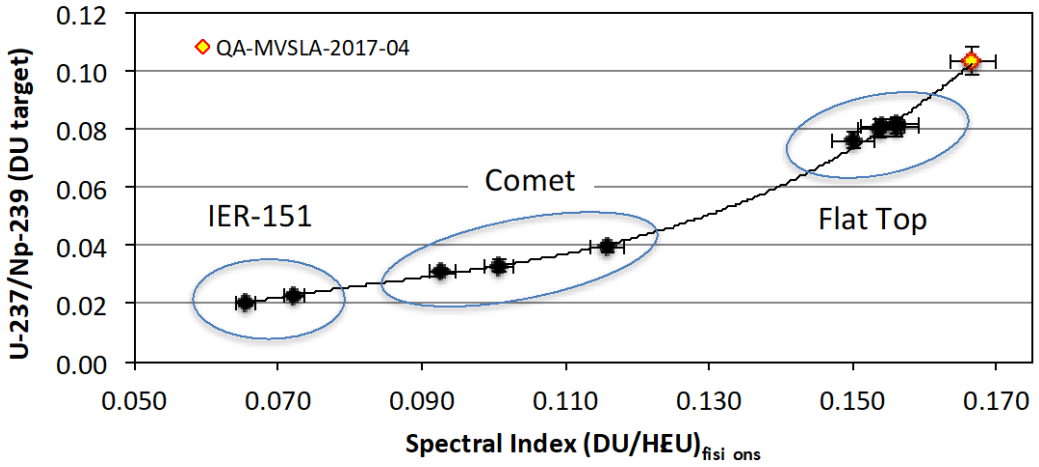

Figure 3. Comparison of recent LANL critical assembly experiments with QA-MVSLA-2017-04

OBSERVATIONS AND LESSONS LEARNED

At LANL, the reported average results for the radiometric measurement of ^{237}U and ^{239}Np and the mass spectrometric measurement of their ^{237}Np and ^{239}Pu daughters matched within uncertainties, demonstrating that the two techniques are on the same atom scale. We note, however, that the replicate values for neptunium measurements, both radiometric and mass spectrometric, for this exercise are much more varied than the uranium or plutonium measurements. For mass spectrometry, the individual replicate 2σ uncertainty bands for ^{237}Np did not overlap. The large variability in the ^{237}Np values could be attributable to poor equilibration of tracer with the samples. As mentioned above, the typical perchloric fuming equilibration step was not done here due to a lack of perchloric hoods in the space needed to handle the high U content. Also the neodymium fluoride precipitation step could have been made more quantitative for Np had iron (II) reducing reagent been added. Despite the variability in the mass spec Np data, there is no apparent bias, or offset from the corresponding radiometric data, as the replicates evenly bracket the radiometric numbers (Figure 4).

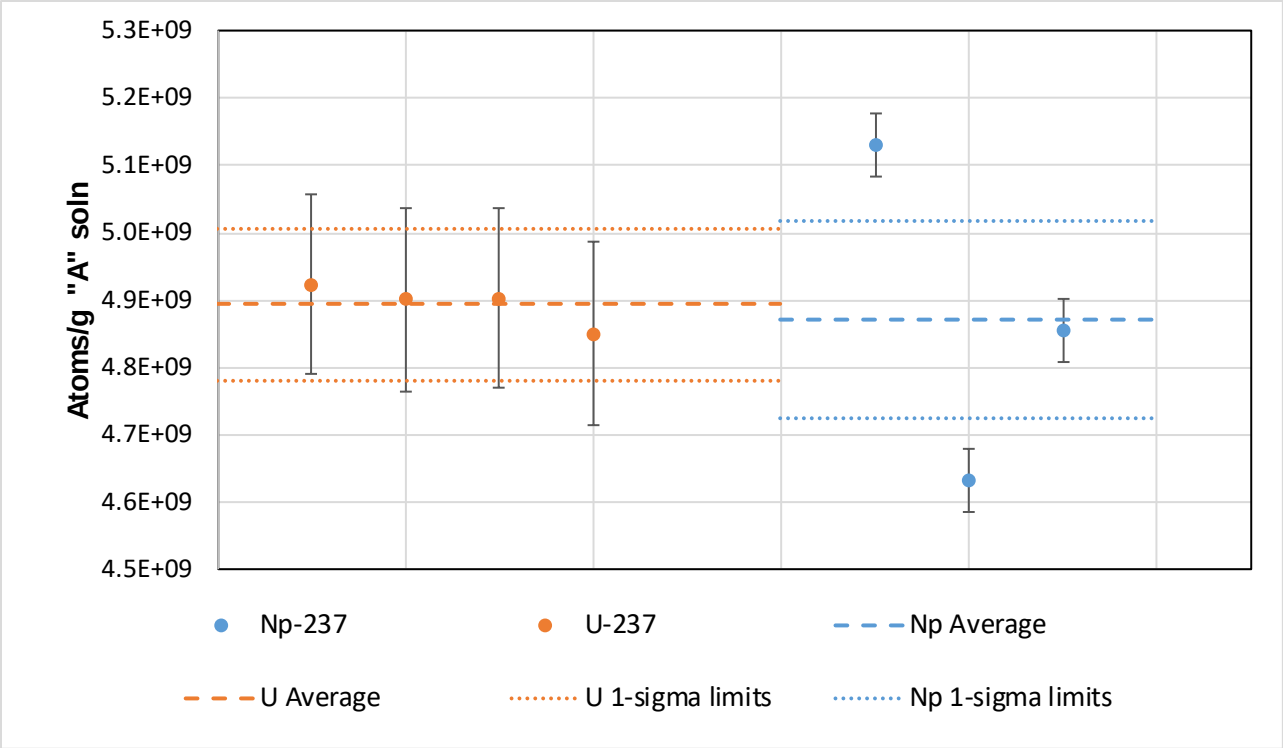

Figure 4: Comparison of replicate radiometric ^{237}U measurements with mass spectrometric measurements of its daughter, ^{237}Np

Similarly for the radiometric ^{239}Np data, there is higher variability compared to the mass spectrometric Pu data (Figure 5). In this case, it might be tempting to suspect a slight low bias in the ^{239}Np relative to the Pu, but given the overlapping 1σ uncertainty bands we can say there is likely not a bias. A simple Student's t-test can be used to evaluate the two populations, which results in the conclusion that the 2 populations are indistinguishable (Table 12).

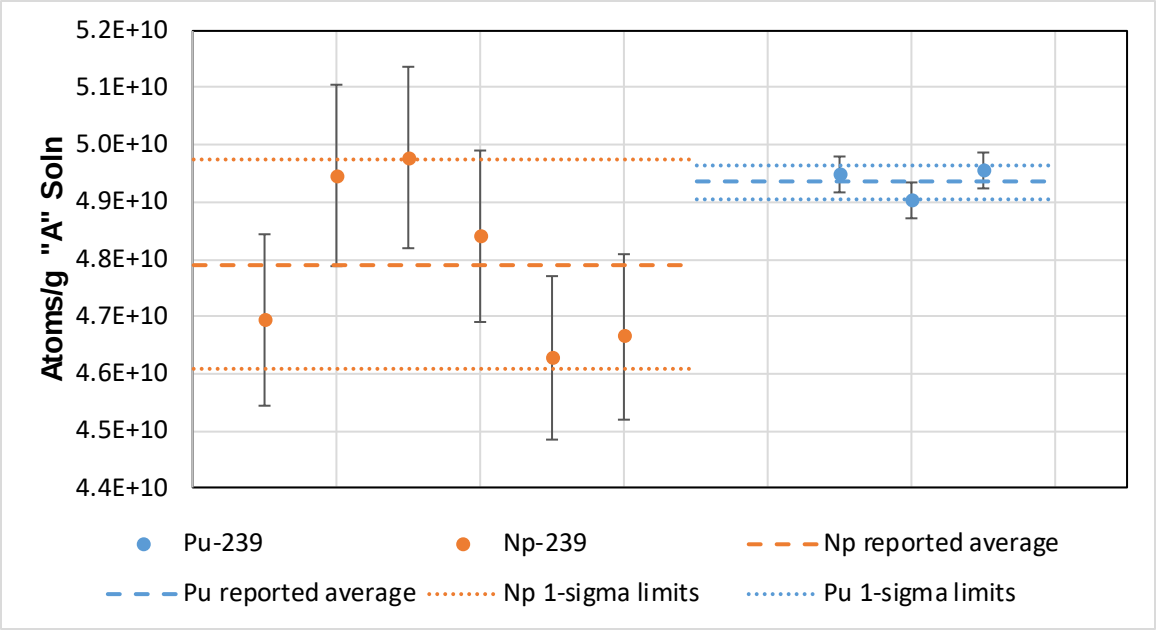

Figure 5: Comparison of replicate radiometric ^{239}Np measurements with mass spectrometric measurements of its daughter, ^{239}Pu

Table 12. Student's t-test for ^{239}Np to ^{239}Pu Populations with Unequal Variances

	Np-239	*Pu-239*
Mean	4.79E+10	4.94E+10
Variance	2.26E+18	8.44E+16
Observations (n)	6	3
Hypothesized Mean Difference	0	
df	6	
t Stat	-2.26849	
P(T<=t) one-tail	0.0319	
t Critical one-tail	1.94318	
P(T<=t) two-tail	0.0638	
t Critical two-tail	2.446912	

t-Stat lies between +/- t Critical for two-tail, so accept the null hypothesis—the means are indistinguishable

The QA-MVSLA-2017-04 test plan specifies radiochemical measurement uncertainty requirements. For the short-lived actinide isotopes the uncertainty objective for the ^{237}U/^{239}Np atom ratio is less than ±1.5%. The actual measured ^{237}U/^{239}Np atom ratio during this exercise was determined as 0.1034 (± 4.5%), in which the measurement uncertainty in ^{237}U was ± 2.3% and in ^{239}Np was ± 3.8%. These measurement uncertainties are normal compared to prior analyses of irradiated DU targets in recent NCERC critical assembly experiments. For example the uncertainty in measured ^{237}U/^{239}Np atom ratios for ten separate experiments conducted between 2012 and 2017 was 4.0 ±0.6 % using identical methods described in this report.

The QA-MVSLA-2017-04 test plan also specifies mass spectrometry measurement uncertainty objectives. The irradiated foil uncertainty requirement is <3% for $^{237}Np/^{239}Pu$ and <3% for ^{239}Pu/fission. Both of these objectives were met for this exercise, at 2.7% and 1.6% respectively. For the unirradiated foil, the objective is listed in the test plan as "the desired MDC should be the same order of magnitude as the uncertainty for measurements of the irradiated DU sample." Given the large difference between atom values for the irradiated and unirradiated foils (over 5 orders of magnitude for ^{237}Np), this objective is somewhat inapplicable (very easy to meet). The uncertainty for measurements of ^{237}Np in the irradiated DU is 1.4×10^8 atoms/g while the MDC for the unirradiated foil is on the order of 10^4 atoms/g A (much much lower). Fortunately, due to the small amount of ingoing analyte contributed by the foil itself before irradiation, there is no need to make a correction to the final measured results in the irradiated sample for the matrix.

CONCLUSIONS

Exercise QA-MVSLA-2017-04 was a success from LANL's perspective. Successes include:

- The irradiation produced ample amounts of both short-lived analytes (^{239}Np and ^{237}U)
- Production of ^{237}U was higher than in comparable experiments with critical assemblies relative to ^{239}Np
- The ingoing analyte concentrations (^{239}Pu and ^{237}Np) from the foil matrix were insignificant relative to how much analyte was produced, thus no correction to final irradiated foil results was required
- LANL's mass spectrometry and radiochemistry teams' results match within reported uncertainties (teams are on the same atom scale)
- All timelines were met

Some areas for improving the process at LANL include finding a space with low Pu and Np backgrounds that will allow handling of high levels of uranium with a perchloric fuming capacity. Np chemistry seems to be the most variable and would likely benefit from the more robust tracer equilibration that perchloric fuming would normally have provided. Our new Building 107 (WAC Refurbishment) may be able to provide this space.

LANL would also like to suggest limiting the number of blanks that become associated with these QA exercises. For this exercise the mass spectrometry team analyzed 4 blanks for 2 samples. The blanks don't contribute much useful data and sometimes make the batch size too large to process all the samples together, doubling the effort required for the exercise.

Overall, LANL found this exercise to be a useful experiment for producing short-lived actinides and practicing our ability to measure them.